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INVESTIGATION OF PLASTICIZERS FOR OIL-RESISTANT RUBBER
FOR SERVICE AT LOW TEMPERATURES
IN CONTACT WITH HYDROCARBON FLUIDS

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PHILLIPS PETROLEUM COMPANY

NOVEMBER 1952

WRIGHT AIR DEVELOPMENT CENTER

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November 1952

*Materials Laboratory
Contract No. AF 33(038)-17201
RDO No. 617-12*

**Wright Air Development Center
Air Research and Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio**

FOREWORD

This report was prepared by Messrs. J. C. Hillyer and C. S. Imig of Phillips Petroleum Company, Bartlesville, Oklahoma, under Contract Number AF 33(038)-17201, Research and Development Order Number 617-12, Compounding of Elastomers. The work was accomplished under the general direction of Mr. W. B. Reynolds. Mr. W. M. Hutchinson assisted with the synthesis work during the early part of this contract and Mr. J. F. Svetlik and co-workers assisted in the evaluation of the products. Work was initiated in January 1951, and was administered under the direction of the Elastomer-Plastics Branch of the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, with Mr. E. R. Bartholomew acting as Project Engineer until October 1951. Lt. D. L. Byerley acted as Project Engineer for the duration of the contract.

ABSTRACT

A review of prior work and available literature on plasticizers in oil-resistant rubber for low temperature applications was made. With respect to compatibility these data indicate that a prospective plasticizer should (1) contain polar groups, (2) have a relatively low molecular weight - about 300, and (3) contain a high percentage of oxygen - about 21 percent or possibly higher.

The following materials were evaluated as low temperature plasticizers for Paracril NS-26; various liquid polybutadienes and their derivatives; the butadiene-furfural cotrimer and several of its derivatives; hydroxylated butadiene derivatives; Polyethylene Glycol derivatives; Thiokol's ZL-109 alone and blended with TP-90B; substituted amides, ureas and urethans, TP-90B derivatives; hydroxynitriles; diallyl sebacate and divinyl benzene as vulcanizable softeners; several silicones; several phosphonate esters; several mercaptan-ethylene oxide condensates; and sorbitol. Of the plasticizers tested most were found unsuitable due either to the failure to improve the low temperature properties over those of the unplasticized stock or to the high extractability from the compounded stock by 70/30 isooctane-toluene mixture. However, several hydroxypolybutadienes containing about 5 to 10 percent oxygen, several ZL-109/TP-90B blends, and N-formyl morpholine showed some promise and these and similar materials should be investigated further, along with the Polyethylene Glycol derivatives which show some promise as a group although no exceptional material has been found in this group as yet.

Several 90/10 copolymers of 1,3-butadiene and 1-cyano-1,3-butadiene prepared from 1-cyanobutadiene containing varying amounts of the cis- and trans-isomers were compounded with 20 phr of TP-90B and with 20 phr of liquid polybutadiene and compared with samples of Paracril B and Paracril 18 which had been compounded similarly. The cyanobutadiene copolymers were in general superior to the Paracrils in low temperature properties but inferior to them in oil-resistance and other physical properties. The copolymers made from cis 1-cyanobutadiene appeared to be the most promising of the experimental copolymers.

PUBLICATION REVIEW

This report has been reviewed and is approved.

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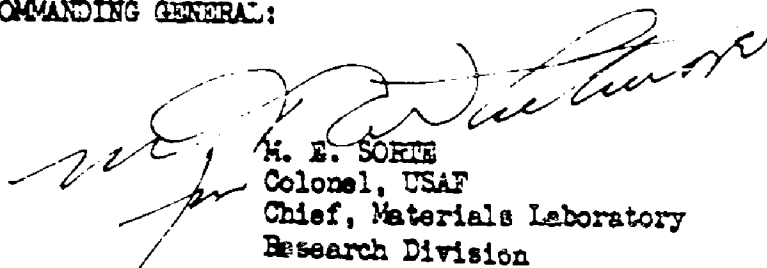

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INTRODUCTION

There is a widespread and critical need in the armed forces for a rubber which retains its elastic properties under arctic conditions and in addition is oil-resistant so that it can be used in continuous service in contact with hydrocarbon fluids. These services include such uses as the liners for self-sealing fuel tanks, gasoline hose lining, gaskets for numerous services, and motor mountings and other machine and ordnance parts.

There are two obvious approaches to this problem. The first and the one with which this contract is chiefly concerned is the development of a plasticizer for existing oil-resistant polymers which will impart the desired properties to the compounded stock. The second is the development of a new, oil-resistant polymer to be used alone or with an appropriate plasticizer. In order that a plasticizer be suitable in either existing or new polymers it should not be extracted from the compounded stock on continuous contact with hydrocarbon fluids, it should be sufficiently non-volatile so that it will not evaporate from the stock during storage, it should exhibit high compatibility with the polymer so that it will not bleed from the stock, and it must impart the desired low temperature flexibility to the finished rubber. Development of a new, oil-resistant elastomer for low temperature applications is being actively studied in a number of laboratories, but this lies outside the scope of this contract. However, some work has been done on plasticizers for a new, oil-resistant copolymer of 1,3-butadiene and 1-cyano-1,3-butadiene.

Types of plasticizers which exhibit high compatibility with acrylonitrile-type rubber are well known and include various esters such as dioctyl phthalate, sebacates and other highly oxygenated compounds. Non-extractable plasticizers have been developed for GR-S polymers, most notable of these being the vulcanizable softener, liquid polybutadiene. Plasticizers that impart good low temperature flexibility to acrylonitrile rubbers have been found in recent studies 1/. Among these are dioctyl and dihexyl sebacate, dicapryl adipate, Carbide and Carbon's Plasticizer 3GH and 3GO, and Thiokol's TP-90B, TP-95 and TP-98. However, no plasticizers have been found which will confer the desired low temperature properties to oil-resistant rubbers and yet remain non-extractable.

Since compatibility of the plasticizer with acrylonitrile copolymers is one of the essential properties, data from several rather extensive studies on the types of plasticizer molecules which are most compatible with acrylonitrile rubbers were examined and carefully correlated.

To achieve non-extractability of the plasticizer in rubber compounds, an obvious approach is the use of a material which is in itself vulcanizable and will, therefore, become an integral part of the rubber during the period of cure. Development of such a vulcanizable plasticizer for ordinary service in both oil-resistant and tire-type polymers has been the subject of a great deal of research. Vulcanization consists of the establishment of cross linkages through sulfur or other atoms between the polymer molecules. In the case of a vulcanizable plasticizer, the cross linking would take place between the softener and the polymer molecules. This results in an increase in the average molecular weight of the polymer.

On the other hand it has been argued that improvement in the low temperature properties of a polymer requires a lowering of the average polymer molecular weight by the additive. The action of a plasticizer in reducing the number of such cross linkages in the original polymer is believed to contribute to the lower degree of rigidity of the structure which is most apparent as the temperature is lowered to near the freeze point.

It might seem, and indeed this position is taken by competent investigators, that good low temperature properties and vulcanizability of the plasticizer are not consistent and cannot be achieved together and that another solution to the problem of extractability of the plasticizer must be made. In view of the rather limited knowledge concerning the action of plasticizers, particularly at low temperatures, it was decided not to abandon the attack upon the problem from this angle and to make at least a brief investigation of certain vulcanizable materials whose composition appeared to offer attractive possibilities.

Another obvious way to achieve non-extractability is by the use of a plasticizer possessing negligible solubility in hydrocarbon fluids and high solubility in the polymer itself. In the case of ordinary butadiene-styrene copolymers which are composed solely of hydrocarbons and thus closely resemble the extracting solvent, the existence of such plasticizers is highly improbable. With the acrylonitrile-butadiene copolymers, it appears that such a plasticizer may exist since this copolymer is no longer strictly a hydrocarbon. It differs in type sufficiently to have very little compatibility with hydrocarbons.

Therefore, this problem was attacked along the following lines:

1. Various liquid butadiene polymers and their derivatives were tested in Paracril NS-26 (Tables I and II, Appendix 2). Various sodium-polymerized liquid polybutadienes of different viscosities were tested along

with several hydrogen fluoride-polymerized liquid polybutadiene and several vinylcyclohexene (butadiene dimer) polymers. Since none of these gave the desired properties alone they were tested in blends with commercial plasticizer TP-90B and Thiokol's liquid polysulfide ZL-109.

2. The butadiene-furfural cotrimer, 2,3,4,5-bis-(Δ^2 -butenylene) tetrahydrofurfural, was tested along with the crude tar from which it was recovered and several materials of intermediate purity (Table IV, Appendix 2). The pure cotrimer was also tested in blends with TP-90B and with a higher sulfur level. Although the pure cotrimer appeared rather interesting at first it was discovered that, due to its volatility, the aliquot method of determining extractability (this method is no longer used) gave erroneous results and the plasticizer was actually rather extractable. Ethylene oxide derivatives and hydroxylated derivatives were also prepared and evaluated.

3. Several derivatives of erythritol and 3-butene-1, 2-diol (products from the hydroxylation of butadiene) were tested (Table VI, Appendix 2) in Paracril NS-26.

4. After preliminary screening tests on a number of Polyethylene Glycol derivatives, several were tested in Paracril NS-26 (Table VII, Appendix 2). These included a number of esters and some cyano derivatives.

5. A rather extensive investigation of Thiokol's liquid polysulfide ZL-109 both alone and blended with TP-90B was made (Table IX, Appendix 2). Several blends were found which appear rather promising.

6. Since dimethylformamide is an effective swelling agent for polyacrylonitrile, it was believed that a plasticizer having the desired properties might be found among various materials containing the amide structure. Several substituted amides and ureas were therefore evaluated in Paracril NS-26 (Table X, Appendix 2). Of the materials tested, one, N-formyl morpholine, exhibited several favorable characteristics which makes further study of this type of compound appear rather interesting.

7. Modifications of TP-90B were made which were expected to reduce the extractability.

8. Unsaturated nitriles were hydroxylated in an effort to reduce their hydrocarbon solubility.

9. Diallyl sebacate and divinyl benzene were tested as vulcanizable softeners in Paracril NS-26 both alone and with benzoyl peroxide or blended with TP-90B (Table XIV, Appendix 2).

10. A recent patent 2/ describes the use of polymeric, non-miscible type plasticizers for various rubbers. In view of this, several silicones which possibly might exhibit plasticizing action but which are known to be incompatible with Paracril NS-26 were tested to determine if these materials would improve the low temperature properties of this rubber.

11. Several other materials, two phosphonate esters, mercaptan-ethylene oxide condensates, and sorbitol, were tested in Paracril NS-26 (Tables XVI and XVII, Appendix 2).

12. A recent report 3/ that a 90/10 copolymer of 1,3-butadiene and 1-cyano-1, 3-butadiene exhibited good low temperature properties and good oil resistance prompted an investigation using this copolymer in which the plasticizer requirements may be less demanding. This report also indicated that the trans-isomer gave a better low temperature copolymer than either the cis-isomer or a mixture of the cis- and trans-isomers. Several samples of copolymers were prepared from samples containing various proportions of the cis and trans-isomers (Table XVIII) for testing as a low temperature, oil resistant elastomer. With 20 phr of plasticizer the cis-isomer appears to give a more promising polymer than the trans-isomer (Tables XIX-XXI, Appendix 2).

SECTION I

METHODS

So long as the usual stress-strain and other physical properties of the rubber product remain within normal limits, little attention need be given to the minor variations which occur within these limits. Primary attention was, therefore, directed toward those properties of the rubber product which reflect its suitability for use in low temperature service while in contact with hydrocarbon fluids and complete physical tests were omitted in many instances. The tests yielding pertinent information concerning the low temperature behavior of these rubber products are the freeze point, cold compression set, swell and extractability. The extractability is a direct measure of one of the integral parts of the problem. In contrast, swell in a 70/30 isooctane-toluene solution is a measure of the compatibility of the plasticized rubber with hydrocarbon fluids and often correlates with the extractability of the plasticizer.

The freeze point indicates the temperature limit at which the polymer may be expected to be plastic and therefore usable. The degree of plasticity at a low temperature (-35°F.) is measured by the cold compression set, for any polymer not frozen at the test temperature gives a good index to the potential value of the compound for various services. These properties together with normal physical properties of the rubber should remain at satisfactory levels after exposure to hydrocarbon fluids. If a prospective plasticizer appears good as a result of the above tests, redetermination of these properties after a so-called cycling operation is important since it will indicate the behavior of the finished rubber after continuous exposure to hydrocarbon fluids.

A. Test Procedures

The test methods employed on the compounded samples were the usual methods in use throughout the rubber industry with a few additions. All the tests were made in the Rubber Evaluation Laboratory located in the Philtex Experiment Station, Phillips, Texas, by experienced test personnel. The equipment and procedures were in exact accordance with those standardized by ASTM Committee D-11.

Specifically, the tests made and the procedures used were as detailed below:

Tensile Strength - Determined by ASTM Method D-412-49T at 80°F. Hot tensiles taken at 200°F.

Elongation - Also determined by Test Method D-412-49T.

Compression Set - Determined by ASTM Test Method D-395-49T. Deflection 35 percent for 2 hours at 212°F. plus 1 hour relaxation at 212°F. Cold compression set taken at 35 percent deflection for 22 hours at -35°F. plus 0.5 hour relaxation at -35°F. This was later carried out in a carbon dioxide atmosphere.

Modulus - Value taken at 300 percent elongation. Test method designated D-797-46.

Freeze Point - Determined by the Gehman apparatus; Test Method D-1053-49T.

Mooney Viscosity - Determined by ASTM Test Method D-927-49T using in general the small rotor at 1.5 minutes (MS 1 1/2).

Shore Hardness - Durometer hardness determined by the shore hardness tester, ASTM Method D-676-49T.

Swell - Determined on the compounded samples by immersion in the 70/30 isooctane-toluene mixture for 72 hours at 157°F. The increase in volume and weight were measured. The solvent and swollen samples were used in extraction test.

Extractability was determined by two methods using the solvent and sample from the swell test. In one method, an aliquot of the solvent was evaporated in a watch glass on a hot plate at very low heat, and the residue weighed. In the alternate method, the swollen rubber was dried in a vacuum oven at 110°F. The difference in weight between the dried sample and the original taken for the swell test was obtained. The loss in weight on extraction was reported as percent of the compounded rubber. Only the weight method is now

being used to determine the extractability of the plasticizer because of the erroneous results obtained in several cases by the aliquot method. Also, the extractability test is now being carried out by immersion of the specimen in 70/30 isooctane-toluene blend for two days at 158°F. then dried three days at 158°F. in accordance with standard Air Force procedure.

The values for this report have been converted to parts per hundred of rubber and then to percent of the original amount of softener added. A correction for the extraction of stearic acid determined on unplasticized samples has been applied.

A TR(Temperature Retraction) test was also employed to measure the freeze point. In this test a 4.0 inch T-50 specimen is extended 50 percent and immersed in a cold bath (-70°F.) of acetone. After three minutes the sample is released and allowed to warm up slowly and the temperatures corresponding to 0,1,2,5,10....90 percent retraction are determined. The freeze point is determined by extrapolating the straight line portion of the temperature versus retraction curve to zero retraction.

Swell in the Plasticizer - The compounds to be tested as plasticizers were screened for compatibility with the rubber products by a swell test in order to eliminate those compounds of very limited compatibility with the rubber products. This test gives an indication of the softening action of the plasticizer. The procedure for this test is described below:

Circular rubber specimens 21 millimeters in diameter and 2.3 millimeters thick were weighed first in air and then in water. The specimen was then dipped in acetone, quickly blotted dry with filter paper, and then immersed in the plasticizer contained in a small vial. The vial was capped and placed in a constant temperature oven maintained at 158°F. After one week the vial was removed from the oven and allowed to cool for 30 minutes. The rubber specimen was then removed, dipped in acetone, blotted dry, and weighed in air and water as before. The volume change was calculated from the change in the difference between the weights in water and air. After dipping in acetone and drying, the specimen was returned to its vial and replaced in the oven. After an additional two weeks, swell was again determined. The specimen was then placed on a piece of filter paper for 24 hours and observations on bleeding were made.

B. Compounding Recipes

In general the following gasket recipe was used:

	<u>PHR</u>
Elastomer	100.0
Philblack A	60.0
Zinc Oxide	5.0
Stearic Acid	1.5
Sulfur	1.5
Antioxidant	1.5
Plasticizer	Variable

The elastomer used was Paracril NS-26 except in the case of the butadiene-1-cyanobutadiene evaluation where this elastomer was compared with Paracril 18 and Paracril B in the above recipe. With 20 or more phr plasticizer, the amounts of sulfur and accelerator were increased to 2.0 and 1.75, respectively. In several other cases, where noted, the sulfur and accelerator levels were increased even more. All results are for a 45 minute cure at 307°F. except where noted.

C. Synthetic Procedures

Standard organic chemical procedures and apparatus were employed in the synthesis of the plasticizers tested and in the preparation of the 1-cyano-1,3-butadiene. Details of these preparations are given in Appendix 1.

D. Polymerization Procedure

The 90/10 copolymer of 1,3-butadiene and 1-cyano-1,3-butadiene was prepared from freshly distilled monomers using the following recipe at 122°F:

	<u>PHR</u>
1,3-butadiene	90.0
1-cyano-1,3-butadiene	10.0
Water	180
OER soap	5.0
K ₂ S ₂ O ₈	0.30
DDM	Variable

The mercaptan level was adjusted to obtain a copolymer of approximately 60 Mooney value and the polymerization was allowed to proceed to about 60 percent conversion. Details of each individual polymerization are given in Table XVIII, Appendix 2.

SECTION II

RESULTS AND DISCUSSION

A. Correlation of Existing Data on Compatibility of Softeners with Various Polymers

This study revealed that plasticizers which were suitable for acrylonitrile copolymers differed markedly from those suitable for less polar rubbers. The common elastomers may be arranged in order of increasing polarity starting with non-polar butyl rubber through natural rubber, GR-S and Neoprene to the most highly polar acrylonitrile rubber (Paracril).

Based on compatibility alone, conveniently determined by a simple swelling test, the following statements summarize our conclusions from this review:

1. The highest compatibility with Paracril is obtained with low molecular weight plasticizers. The available data on several series of ester type plasticizers including fatty acid esters, dibasic acid esters, and long chain glycols show that the compatibility increases with a decrease in molecular weight and increases very sharply below a molecular weight of about 500.
2. Highly polar plasticizers are more compatible than less polar or non-polar plasticizers with Paracril rubber. Thus, hydrocarbons in general cause very little swelling of Paracril while esters of dibasic acids cause more swelling than esters of monobasic acids.
3. Since oxygen is the element most frequently present to give polarity to the plasticizers, a rough correlation can be shown between the degree of swell as a measure of compatibility and the oxygen content expressed as the number of oxygen atoms or percent oxygen. For Paracril rubber, the data show that, for plasticizers of equal numbers of carbon atoms and of approximately equal molecular weights, the swelling action increases with increasing numbers of oxygen atoms up to at least seven. Above seven oxygen atoms per molecule so few compounds have been investigated that the apparent leveling off of the amount of swell may not have any significance.

In this correlation, the oxygen atoms have all been regarded as equivalent in producing polarity, an obvious inadequacy. Carbonyl, hydroxyl and ester oxygens probably contribute differently to the plasticizing action. Possibly both oxygens in an ester or carboxyl group should be counted as one; i.e., the number of polar groups rather than the individual oxygen atoms should be considered. Those plasticizers which are the best swelling agents for Paracril rubber were all found to contain above 30 percent oxygen.

4. Not all polar groups are necessarily equivalent. With Paracril it can be shown that a plasticizer having polar groups on adjacent carbons is a much poorer swelling agent than a plasticizer in which the polar groups are widely separated. The effect is very marked in low molecular weight compounds but becomes negligible with quite high molecular weight compounds.

5. There is evidence that the low temperature properties of Paracril are improved (T_{10} , T_x , and brittle points lowered) with increasing oxygen content of the plasticizer up to about 25 percent oxygen but not above this point. Satisfactory results probably can not be expected from a plasticizer which itself crystallizes or gels at the test temperature; it may be that the more highly oxygenated compounds containing six or seven oxygen atoms are subject to this defect.

B. Polybutadiene and Polybutadiene Derivatives as Plasticizers in Paracril NS-26. (Tables I, II and III, Appendix 2).

Sodium-polymerized liquid polybutadienes of various viscosities were tested as plasticizers in Paracril NS-26. When comparing these plasticizers it can be seen that in general as the viscosity of the polybutadiene increases the freeze point of the plasticized stock approaches that of the unplasticized stock and the extractability decreases. Little can be determined from the cold compression set data since the stocks were practically all frozen at the test temperature, -35°F . It might appear at first glance that a liquid polymer of the proper viscosity to give the best balance of properties might be desirable. However, it is believed that even if we could approach the low temperature properties of the low viscosity material and the extractability of the high viscosity material, the resulting material would still not have sufficient action to make it suitable under the desired conditions. A blend of TP-90B with the low viscosity material gave slight improvement in the low temperature properties but also increased the extractability.

Hydrogenated liquid polybutadienes (low viscosity) did not appear to impart low temperature properties superior to those imparted by the original polymer; however, it did appear to increase the extractability considerably. Blending this hydrogenated material with TP-90B greatly improved the low temperature properties but also increased the extractability of the compounded stock. A blend of this material with ZL-109 both decreased the extractability and improved the low temperature properties somewhat over the stock plasticized with hydrogenated polybutadiene alone.

The hydrogen fluoride-polymerized polymer had much the same effect on the low temperature properties as did the sodium-polymerized polymer. It exhibited much higher extractability, thus making it inferior to the sodium-polymerized polymer. The vinylcyclohexene polymer (polymerized by phosphorus pentoxide) showed no improvement in low temperature properties of the compounded rubber and was, in addition, completely extracted, thus making it inferior to both of the other two types of polymers.

Of the several hydroxypolybutadienes evaluated in Paracril NS-26 a few have shown some promise. Attempts to duplicate these results thus far have failed. It should be noted in Table II that as the amount of oxygen is increased the extractability is reduced along with a corresponding increase of the freeze point while the cold compression set remains essentially the same. This indicates that stock containing any of the hydroxypolybutadienes, although they may appear to be somewhat flexible at -35°F ., are almost completely frozen after longer exposure at this temperature. Modification of the hydroxypolybutadiene molecule by esterification or condensation with ethylene oxide in several cases reduced the extractability but gave no improvement in low temperature properties over the unplasticized stock. Oxidation of liquid polybutadiene-producing mainly ketonic oxygen - gave a product which was comparable to hydroxypolybutadiene in low temperature properties but inferior to it insofar as extractability is concerned.

C. Butadiene-Furfural Copolymers as Plasticizers in Paracril NS-26 (Tables IV and V, Appendix 2).

The pure cotrimer, 2,3,4,5-bis-(Δ^2 -butenylenes) tetrahydrofurfural, appeared rather promising since, even though it was somewhat inferior to the control softener TP-90B in regard to low temperature properties, it was considerably better insofar as extractability was concerned. However, it was later learned that the aliquot method of determining extractability was giving erroneous results due to the volatility of the plasticizer itself and that this material was nearly as extractable as TP-90B. Blending this plasticizer with TP-90B imparts better low temperature properties than the cotrimer alone, but the extractability is too high to make this a suitable plasticizer for oil-resistant rubber.

A study of this material of various stages of purity from the crude tar to the pure cotrimer indicates that the freeze point of the plasticized stock decreases with increasing purity while the cold compression set and extractability remains essentially the same for all the materials except the crude tar.

Reduction of the pure cotrimer to its corresponding alcohol, contrary to expectations, did not appreciably reduce the extractability and in addition did not materially affect the low temperature properties of the unplasticized stock. Subsequent condensation of this alcohol with ethylene oxide did improve the extractability but had little effect on the cold temperature properties. Hydroxylation of both the cotrimer itself and its corresponding alcohol yielded materials which were essentially non-extractable but which did not improve the low temperature properties.

D. Hydroxylated Butadiene Derivatives as Plasticizers in Paracril ES-26
(Table VI, Appendix 2).

All of the plasticizers of this type that were tested gave poor low temperature properties and all but the residues from the erythritol preparation and the polyesters were almost completely extracted. It should be noted that the aliquot method of determining extractability may not be applicable to the erythritol residues and may be giving erroneous results. The polyesters function well as non-extractable softeners but as mentioned above do not improve the low temperature properties.

E. Polyethylene Glycol Derivatives as Plasticizers in Paracril ES-26
(Tables VII and VIII, Appendix 2).

As a result of preliminary screening tests several Polyethylene Glycol derivatives were tested in Paracril ES-26. The mono esters of Polyethylene Glycol 200 were effective in improving the low temperature properties of the rubber (although not as effective as TP-90B) but were quite extractable and in addition exhibited only limited compatibility with the elastomer. An experimental blend of two of these esters with Polyethylene Glycol 400 was made to obtain a material containing the minimum amount of glycol to render the blend insoluble in 70/30 isooctane-toluene and to give a minimum freeze point. This material (4616-26) was unsuitable due to its incompatibility with the elastomer in question. The high extraction values may be explained by the incompatibility of this blend with the compounded stock and the resultant bleeding gave the erroneous results. The diesters tested showed the same general properties except the mixed adipate which exhibited greater compatibility. Introduction of cyanoethyl groups did not appear to improve the low temperature properties, extractability or compatibility.

F. Blends of ZL-109 and TP-90B as Plasticizers in Paracril ES-26 (Table IX, Appendix 2).

Preliminary results indicated that ZL-109, although not a suitable plasticizer itself, may advantageously be used blended with one or more other plasticizers; therefore, a rather extensive study of blends of ZL-109 and TP-90B was undertaken. Since the blends were retarded in cure, the sulfur and accelerator levels were increased and a 75 minute cure time was used. Examination of the compression set data, however, indicates that increasing the sulfur and accelerator levels seems to lower rather than increase the state of cure. Blending with TP-90B showed the same general trends as observed before, improved low temperature properties and increased extractability. It is significant, however, that some blends compare favorably with TP-90B in low temperature properties but are much less extractable. It should also be noted that in several cases better cold compression set values were obtained

for a 75 minute cure. Even though the 10 second recovery values for the cold compression set are rather poor, spot readings after one minute relaxation show that recovery is rather rapid after a slow start. High loadings of ZL-109 had a very deleterious effect on the tensile strength and elongation.

G. Amide-Type Plasticizers in Paracril NS-26 (Tables X and XI, Appendix 2)

It appears that n-octyl urea does not improve the low temperature properties of Paracril NS-26 thus making it inferior to the control, TP-90B, even though it is somewhat less extractable. Blends with TP-90B also showed little promise.

A comparison of 4843-17, diethanolformamide, and 4843-25, N-formyl morpholine, is rather interesting. It can be seen that the former is quite incompatible, has no effect on the low temperature properties and is only slightly extractable. However, the latter, which is structurally similar to the 4843-17 in that it is the product which would result from the cyclic dehydration of 4843-17, shows no sign of incompatibility and appears rather effective in improving the low temperature properties but is somewhat more extractable. It should be noted that N-formyl morpholine was effective in improving the low temperature properties in spite of the fact that it melted at 66°F. It is believed that further investigation of materials similar to N-formyl morpholine would prove quite interesting.

Neither Eyn-H, N-diethanolurea nor N-hydroxyethylurethan appear to improve the low temperature properties of Paracril NS-26 very much and in addition both were highly extracted from the compounded stock.

H. TP-90B Derivatives as Plasticizers in Paracril NS-26 (Table XII, Appendix 2).

Reaction of the hydroxyl groups in TP-90B with m-tolylene diisocyanate gave a product which had improved extractability but inferior low temperature properties as compared to TP-90B. Modification by reaction with succinic anhydride gave a product which imparted low temperature properties comparable to TP-90B; the extractability, contrary to expectations, was increased.

I. Hydroxynitriles as Plasticizers in Paracril NS-26 (Table XIII, Appendix 2).

Hydroxylation of Amels, nitriles, derived from fatty acids, slightly improved the low temperature properties of the plasticized stock. However, contrary to expectations, their extractability was nearly as high as that of TP-90B.

J. Vulcanizable Plasticizers in Paracril NS-26 (Table XIV, Appendix 2).

Both diallyl sebacate and divinyl benzene were evaluated as softeners for Paracril NS-26. Diallyl sebacate effectively reduced the freeze point of the rubber but did not greatly effect the cold compression set and remained highly extractable. It is interesting to note that treatment with benzoyl peroxide had little or no effect on the physical properties. As shown by the data on the extracted stock, any beneficial effect which this material might have had on the elastomer was completely lost after extraction. The lower cold compression set values may be due to some softening action exerted by residual hydrocarbon from the extraction. Divinyl benzene, both alone and blended with TP-90B, was unsatisfactory due to its rather slight effect on the low temperature properties of the rubber even though it is appreciably less extractable than TP-90B alone.

K. Silicones as Plasticizers in Paracril NS-26 (Table XV, Appendix 2).

Two silicones were evaluated as plasticizers for Paracril NS-26 even though it was known they were incompatible with Paracril NS-26. As suggested by a recent patent 2/, it was believed that they were of high enough molecular weight to form a stable mixture with Paracril NS-26. As expected these materials were virtually non-extractable but they did not appear to improve the low temperature properties over those of the unplasticized stock. It should be noted also that the desired physical mixture apparently was not obtained.

L. Phosphonates as Plasticizers in Paracril NS-26 (Table XVI, Appendix 2).

Evaluation of diisooctyl phenylphosphonate and diisooctyl styrylphosphonate in Paracril NS-26 showed that these substances, although somewhat effective in reducing the cold compression set, were almost completely extracted from the compounded stock.

M. Mercaptan-Ethylene Oxide Condensation Products Plasticizers in Paracril NS-26 (Table XVII, Appendix 2).

Plasticizers prepared by condensation of tert-dodecyl mercaptan with one and with nine moles of ethylene oxide were evaluated in Paracril NS-26 and found to be unsuitable as low temperature plasticizers since neither significantly improved the low temperature properties over those of the unplasticized rubber.

N. Sorbitol as a Plasticizer in Paracril NS-26 (Table XVII, Appendix 2).

Sorbitol was evaluated alone and blended with TP-90B in Paracril NS-26. When used alone it was relatively non-extractable but failed to improve the low temperature properties as compared with the unplasticized stock. Blending with TP-90B showed the usual slight improvement of cold temperature properties and the corresponding increase in extractability.

C. 90/10 Butadiene-1-Cyanobutadiene Copolymers (Tables XVIII-XXI, Appendix 2)

A number of 90/10 butadiene-1-cyanobutadiene copolymers have been prepared from 1-cyanobutadiene containing varying amounts of the cis- and trans-isomers. Due to the small amount of elastomers available for evaluation the uncompounded Mooney value (ML-4) was determined on only one blend. This blend, CNBD-1, gave a value of 119 ML-4; however, this value is doubtful because the Mooney reter slipped in the determination. The experimental copolymers were tested with 20 phr TP-90B and liquid polybutadiene and compared with Paracril 18 and Paracril B. The 1-cyanobutadiene copolymers were inferior to the Paracril controls in compression set (212°F.), hydrocarbon resistance, tensile strength, and elongation. The stocks had about equal hardness while the experimental copolymers were superior to the controls in freeze point and cold compression set. It should be noted that the TP-90B was essentially completely extracted out of all the stocks whereas the liquid polybutadiene was appreciably less extractable out of the controls than from the experimental copolymers. Of the experimental copolymers, the one prepared from cis-1-cyano-1,3-butadiene appeared more promising than either the trans-isomer or the mixture of the cis- and trans-isomers. The trans-isomer gave a copolymer which gave only slightly better low temperature properties than Paracril 18 while being much less hydrocarbon resistant. Variation of the cure time showed no significant trends for the experimental copolymer.

SECTION III

CONCLUSIONS

From the foregoing results the following conclusions may be drawn:

1. All the liquid polybutadienes and derivatives which were tested were unsuitable as low temperature plasticizers for Paracril NS-26 except some hydroxypolybutadienes containing about 5 to 10 percent oxygen.
2. All the butadiene-furfural copolymers and derivatives tested were unsuitable as low temperature plasticizers for Paracril NS-26.
3. All the hydroxylated butadiene derivatives tested were similarly unsuitable as low temperature plasticizers.
4. All the Polyethylene Glycol derivatives tested were unsuitable but further investigation of these types of compounds may be warranted.
5. Several blends of ZL-109 and TP-90B showed some promise as low temperature plasticizers for Paracril NS-26 and may warrant further investigation.
6. Of the amide-type plasticizers tested only N-formyl morpholine has shown promise; however, this field should certainly be investigated further. In addition, it appears that a low freezing plasticizer is not required to impart good low temperature properties.
7. Modification of TP-90B by reaction with m-tolylene diisocyanate or succinic acid did not yield a suitable low temperature plasticizer.
8. Hydroxylated nitriles, sorbitol, vulcanizable materials such as diallyl sebacate, phosphonate esters, and incompatible silicones were all found to be ineffective.
9. The ethylene oxide condensates of tert-dodecyl mercaptan were unsuitable as low temperature plasticizers for Paracril NS-26. However, further investigation of ethylene oxide condensates appears desirable.
10. Experimental 90/10 copolymers of 1,3-butadiene and 1-cyano-1,3-butadiene prepared with 1-cyano-1,3-butadiene containing varying amounts of the cis- and trans-isomers, when plasticized with 20 phr TP-90B or liquid polybutadiene, were in general superior in low temperature properties to both Paracril B and Paracril 18 containing the same softener but were inferior to both in oil-resistance and stress-strain properties. The copolymer prepared from the cis-isomer gave the best low temperature polymer while the copolymer prepared from the trans-isomer appeared only slightly better than Paracril 18. Further investigation of copolymers containing the cis- and/or the trans-isomers of 1-cyano-1,3-butadiene appears desirable.

APPENDIX I

SYNTHETIC METHODS

A. Modification of TP-90B

1. Reaction with m-Tolylene Diisocyanate

Into a 500 milliliter three-neck flask equipped with a stirrer, dropping funnel and thermometer was placed 163 grams of TP-90B. Fifty-eight grams of m-tolylene diisocyanate was added dropwise over a 40 minute period. The heat of reaction maintained the temperature between 120-140°F. The viscosity of the mixture increased rapidly; after one hour stirring was no longer possible. When heated to approximately 280°F. a liquid phase separated which did not solidify on cooling. This liquid had the odor of TP-90B. The solid material was recovered by filtration, ground in a mortar, dried at room temperature under a vacuum for several hours, and submitted for testing as sample NES-1.

2. With Succinic Anhydride

Into a 500 milliliter flask which was equipped to remove water was charged 200 grams of TP-90B and 14 grams (10 percent excess based on a hydroxyl number of 71) of succinic anhydride. The temperature was maintained at 392°F. for 36 hours; however, no sign of reaction was noted after 12 hours. A dark brown, rather viscous liquid was obtained which was submitted for testing as sample 4618-9.

B. Butadiene-Furfural Cotrimer Derivatives

1. 2,3,4,5 bis-(Δ^2 -butenylene) tetrahydrofurfuryl alcohol

In a 5-liter three-neck flask equipped with a stirrer, reflux condenser and dropping funnel were mixed 500 grams of potassium hydroxide and 750 milliliters of methanol. After cooling to 130°F. a mixture of 612 grams of the butadiene-furfural condensation product, 800 milliliters of methanol, and 330 milliliters of a 40 percent aqueous formaldehyde solution was added over a 30 minute period while maintaining the temperature between 115-130°F. After four hours at 136°F., stirring was stopped and one liter of water was added. The dark brown lower layer was separated, and after stripping the methanol from the aqueous phase, it was washed with three 400-milliliter portions of benzene. The benzene extracts were combined with the product layer, filtered through Celite and fractionated through a glass column packed with stainless-steel helices. The boiling range was 240-275°F. at one millimeter pressure. This product was submitted for testing as sample BF-7.

2. Ethylene Oxide Condensate of the Above Alcohol.

A solution of 150 grams (0.729 moles) of the alcohol in 150 grams of n-heptane and 7.3 grams of a 20 percent sodium hydroxide in methanol were charged to a half-gallon, stainless-steel, jacketed autoclave equipped with a stirrer and heated to 250°F. A solution of 128 grams (2.91 moles) of ethylene oxide in 128 grams of n-heptane was then pressured into the reactor with nitrogen in small portions over a 2-hour period at a temperature of 238 - 256°F. and a pressure of 18-45 psig. The reaction was allowed to proceed until the pressure dropped to the initial value (18 psig). The product layer was separated from the heptane layer and washed first with water and then with a large portion of benzene. The combined benzene extracts were then dried over potassium carbonate, filtered and the benzene removed by distillation to a final temperature of 212°F. at one millimeter pressure. This product was found to have added an average of three moles of ethylene oxide per mole of alcohol and was submitted for testing as sample BF-8.

C. Hydroxynitriles

1. Hydroxylation of Arneel TOD with Performic Acid

Into a 2-liter flask fitted with a stirrer and thermometer were placed 278 grams of Arneel TOD (the nitrile derived from tall oil), 342 grams of a 25.8 percent hydrogen peroxide solution, 59.3 grams of formic acid, and 100 grams of water. This corresponds to 1.5 moles of hydrogen peroxide per 0.5 mole of formic acid per mole of double bonds in the nitrile. This was maintained at 140°F. and stirred vigorously for 23 hours at which time the theoretical amount of hydrogen peroxide had been consumed. The product was then extracted with benzene, washed with water, sodium bicarbonate solution, and again with water, dried over magnesium sulfate and the benzene removed by distillation to a final temperature of 243°F. at one millimeter pressure. The resulting liquid, which froze at -40°F. was submitted for testing as sample M-19-81.

2. Hydroxylation of Arneel SD with Performic Acid

The hydroxylation was run in the same manner as above except the ratio of the reactants was changed to 3.0 moles of hydrogen peroxide and 3.0 moles of formic acid per mole of the Arneel. The reaction was allowed to proceed for 23 hours at approximately 120°F. after which time the product was recovered as in the preceding preparation. This product was submitted for testing as sample M-615-10.

D. Ethylene Oxide Condensate of Thiokol LP-8

Into a half-gallon, stainless-steel, jacketed autoclave equipped with a stirrer were charged 150 grams (0.5 moles) of Thiokol LP-8, 10 grams of a 20 percent solution of potassium hydroxide in methanol, and 600 grams of n-heptane. After heating to 260°F., 176 grams (4.0 moles) of ethylene oxide in 176 grams of n-heptane was pressured into the reactor in small portions. The reaction proceeded for 6 hours at 258 - 265°F. and at 52 - 90 psig. The heptane insoluble material was then separated, filtered, and stripped to remove any residual heptane. This product, which froze at -96°F., was submitted for testing as sample 4618-34.

E. Esters of Polyethylene Glycols

1. Monooesters of monobasic acids

In all cases equimolar quantities of the acid and glycol were placed in a flask equipped with a reflux condenser and a trap to collect water. A small amount of calcium hydroxide was added and the temperature was maintained at about 350°F. until there was no further sign of reaction. The acid numbers of the resulting products were about 20 milligrams of potassium hydroxide per gram of sample and were undoubtedly too high due to saponification during titration.

2. Diesters of monobasic acids

The acetate esters were prepared by refluxing for 25 hours the glycol with an excess of acetic anhydride containing a small amount of pyridine. The excess acetic anhydride and pyridine were then removed by distillation. The mixed ester of lauric and acetic and Carbowax 1500 was prepared by reacting the monolaurate, prepared as in the foregoing preparation, with an excess of acetic anhydride containing a small amount of pyridine. After allowing this to reflux for 27 hours, about 75 milliliters of water and 100 milliliters of benzene were added. The benzene layer was then separated and the benzene removed by distillation.

3. Esters of dibasic acids

The reaction was carried out in the same manner as in the preceding preparations except that a ratio of 2 moles of glycol to one mole of dibasic acid was used.

F. Ester-Type Plasticizers

1. Polyethylene Glycol 200 Monobutyrate

Into a one-liter flask equipped with a reflux condenser and a trap to remove water from the reflux were charged 300 grams (1.5 moles) of Polyethylene Glycol 200, 132 grams (1.5 moles) of n-butyric acid and 0.02 grams

of calcium hydroxide. The reactants were refluxed for 30 hours at 347°F.; the water formed was removed by means of the above mentioned trap. The product was allowed to cool to room temperature. Nitrogen was bubbled through the product for the first five minutes of the cooling process to aid in the complete removal of water. This material was submitted for testing as sample 4618-28.

2. β -Cyanoethyl Ether of Polyethylene Glycol 200 Monobutyrate

Into a 500-milliliter three-neck flask equipped with a dropping funnel, stirrer and thermometer were placed 150 grams (0.75 mole) of Polyethylene Glycol 200 and 10.2 grams (5.36 percent) of a 40 percent aqueous potassium hydroxide solution. While stirring vigorously 39.8 grams (0.75 mole) of freshly distilled acrylonitrile was added dropwise at the rate of 60 to 80 drops per minute while the reaction was maintained at 85-95°F. After the addition was completed (0.5 hours), the reactants were stirred vigorously while maintaining the temperature at 90°F. The potassium hydroxide was then neutralized with dilute hydrochloric acid and 66.1 grams (0.75 mole) of *n*-butyric acid was added. A reflux condenser with a trap to remove water was added to the flask, and the mixture was maintained at 293°F. for 24 hours. An additional 19.2 grams of *n*-butyric acid was then added, and after maintaining at 293°F. for another 48 hours, the excess butyric acid was removed by stripping at a final pressure of approximately one millimeter for 3 hours. About 20 grams of material was recovered by this stripping process. The product was submitted for testing as sample 4618-49.

3. Esters of Dibasic Organic Acids

In all cases the acid and alcohol in a mole ratio of 1 to 2 were placed in a flask equipped with a reflux condenser and a trap to remove water from the reflux and heated at 302-347°F. for 24 to 48 hours. A small amount of trifluoroacetic anhydride was added to the di-(Methoxy Polyethylene Glycol 350) adipate reaction mixture and xylene was added to the di-(Methyl Carbitel) oxalate reaction mixture to aid in the removal of water.

4. Mixed Esters of Dibasic Organic Acids

In the case of both esters prepared, equimolar quantities of alcohol and acid were heated at 255-350°F. for 8-17 hours in a three-neck flask equipped with a stirrer, thermometer, and a reflux condenser and trap to remove water from the reflux. An equimolar quantity of the second alcohol was then added and the reaction maintained at 300-350°F. for 2 to 24 hours. In one case some purification was achieved by extraction with both hydrocarbon and water.

5. The n-Hexyl Ether of Polyethylene Glycol 200 Mono-(ethyl carbonate).

Into a 500-milliliter three-neck flask equipped with a stirrer, thermometer, and reflux condenser with a vent line for effluent gas were placed 17.4 grams of ethyl chlorocarbonate and 53.8 grams for the n-hexyl ether of Polyethylene Glycol 200, the preparation of which is described below. The reaction was allowed to proceed for 8 hours at 212°F.

6. Tri-(butyl Carbitol) phosphate.

Into a 500-milliliter three-neck flask equipped with a thermometer, stirrer and reflux condenser fitted with a calcium chloride drying tube and vent line for effluent gas were placed 162 grams (1.0 mole) of butyl Carbitol and 51 grams (0.33 mole) of phosphorous oxychloride. The reaction was allowed to maintain itself at approximately 115°F. for one hour. The mixture was then heated and maintained at 212°F. for 4 hours and finally at 302°F. for 16 hours. The mixture was then allowed to cool in an atmosphere of carbon dioxide. This partially solid product was readily soluble in the 70/30 isooctane-toluene solvent.

G. Ether-Type Plasticizers.

1. Acrylonitrile Condensates with Polyethylene Glycols.

In both cases the glycol and about 5 percent of a 40 percent aqueous potassium hydroxide solution were placed in a three-neck flask equipped with a stirrer, thermometer and dropping funnel. An equivalent quantity of acrylonitrile was added dropwise at the rate of 60 to 80 drops per minute while maintaining the temperature at 85-95°F. After the addition was complete, the mixture was maintained at about 85°F. for 6 to 20 hours after which time the mixture was neutralized with dilute hydrochloric acid and the product recovered by vacuum distillation.

2. The Mono-(n-hexyl) Ether of Polyethylene Glycol 200.

Into a one-liter four-neck flask equipped with a dropping funnel, stirrer, thermometer and a reflux condenser fitted with a calcium chloride drying tube and vent line for effluent gas was placed 306 grams (3.0 moles) of n-hexyl alcohol and 5 milliliters of pyridine. While stirring vigorously, 357 grams (3.0 moles) of thionyl chloride was added dropwise while maintaining the temperature at about 85°F. After the addition was complete (4 hours), the reactants were maintained at 120°F. for two additional hours. The dark reaction mixture was then filtered through Celite and washed twice with ice water. The n-hexyl chloride was recovered by distillation (boiling range 268-271°F).

Into a liter, three-neck flask equipped with a stirrer and vent line for effluent gas was placed 242 grams (1.21 moles) of Polyethylene Glycol 200. While stirring vigorously, 29.2 grams (1.27 moles) of sodium was added in small pieces. Dioxane was added to aid in dissolving the precipitated sodium salt. The mixture was allowed to reflux for 3.5 hours. After cooling to room temperature, 145 grams (1.21 moles) of *n*-hexyl chloride was added and the mixture refluxed 5 hours. The mixture was then heated with activated charcoal, filtered through Celite, stripped to remove the dioxane, washed twice with *n*-heptane and stripped to remove any residual heptane. This material was tested as number 4618-68.

H. Acetal-Type Plasticizers.

1. Di-("Ethoxy Triglycol") Formal

Into a 500 milliliter three-neck flask equipped with a gas inlet tube, thermometer, stirrer, and reflux condenser fitted with a vent line for effluent gas were placed 267 grams (1.5 moles) of "Ethoxy Triglycol" and 22.5 grams of trioxane. The reactants were stirred vigorously and maintained at 258°F. for 5 hours while dried hydrogen chloride gas was bubbled through the solution. Nitrogen was then bubbled through the solution in place of hydrogen chloride and the reaction maintained at 285°F. for an additional 15 hours. This material was tested as sample 4618-75.

2. The Mixed Formal of Methoxy Polyethylene Glycol 350 and *n*-Hexyl Carbitol.

Into a liter, three-neck flask equipped with a gas inlet tube, thermometer, stirrer, and reflux condenser fitted with a vent line for effluent gas were placed 350 grams (1.0 mole) of Methoxy Polyethylene Glycol 350 and 30 grams (0.33 mole) of trioxane. The reaction mixture was stirred vigorously while dried hydrogen chloride was bubbled through the solution for 24 hours at 75 - 85°F. After this time 190 grams (1.0 mole) of *n*-hexyl Carbitol was added and the temperature raised to 130°F. After an additional 8 hours nitrogen was bubbled through the solution in place of hydrogen chloride and the reaction maintained at 130°F. for an additional 18 hours. The crude reaction product was then washed with heptane, dissolved in toluene and washed with a saturated aqueous calcium chloride solution, and the toluene removed by stripping. This material was tested as number 4618-80.

I. Oxidized Liquid Polybutadiene.

Into a three-liter, three-neck flask equipped with a stirrer, inlet tube and reflux condenser fitted with a vent line for effluent gas were placed 360 grams of Serial #8 liquid polybutadiene, 1520 grams of toluene, and

5 grams of 70.2 percent cumene hydroperoxide. Oxygen was introduced slowly, just above the stirring paddle and the reaction maintained at 200°F. for 21 hours. The addition of oxygen was then discontinued, the reaction mixture refluxed for 24 hours to decompose the peroxides and stripped to remove the toluene. This material was tested as number 4618-58.

J. Diethanolformamide

Ethyl formate was added to an equimolar quantity of diethanolamine and allowed to stand about 16 hours at room temperature. The reaction was exothermic at first. The reactants were then heated until the reflux vapor reached 170°F. at which time ethyl alcohol was removed by distillation. The product was insoluble in 70/30 isooctane-toluene and froze at -66°F. It was submitted for evaluation as 4843-17.

K. Preparation of β -Hydroxyethylurethan

Ethyl chloroformate (248 grams) was added dropwise with continuous stirring to a mixture of 280 grams of ethanolamine and 400 milliliters of absolute ether at the rate of about 40-45 drops per minute while controlling the temperature at 25 to 40°F. After the addition was complete the mixture was allowed to stand for about 16 hours. The ethanolamine hydrochloride formed was removed by filtration and the filter cake was washed with two 100-milliliter portions of ether. The ether washings were combined with the filtrate and the ether removed by distillation. The residue was then distilled under vacuum and the material boiling at 215.6-217.4°F. at 1 millimeter pressure was collected. A yield of 253.5 grams of liquid which froze at -76°F. and was insoluble in 70/30 isooctane-toluene was obtained. This material was submitted for testing as sample 4843-21.

L. Preparation of Sym-N,N' - Diethanolurea

One mole (128 grams) of β -hydroxyethylurethan was mixed with 1 mole (61 grams) of ethanolamine, heated at 212°F. for 2 hours and distilled. The crude material was distilled and the product fraction was redistilled. The material boiling at 248 to 253°F. at one millimeter pressure was collected. The product, amounting to 82 grams, was a liquid which froze at -66°F.

M. Preparation of N-Formyl Morpholine

Ethyl formate (1.5 moles) was mixed with 1.5 moles of morpholine and refluxed until the reflux temperature reached 175°F. The mixture was then

distilled and the portion boiling at 437-455°F. was collected. A yield of 110 grams of material which melted at 66°F. and was insoluble in 70/30 isooctane-toluene was obtained. This material was submitted for testing as sample 4843-25.

E. Monomers.

1. 1-Cyano-1,3-Butadiene

The 1-cyano-1,3-butadiene was prepared by the pyrolysis of crotonaldehyde cyanohydrin benzoate which had been previously prepared from crotonaldehyde, benzoyl chloride and sodium cyanide 4/.

Into a 22-gallon, glass-lined, jacketed reactor equipped with an anchor-type stirrer, thermowell, inlet and vent lines were charged 2 gallons of technical grade benzene, 2 gallons of reagent grade toluene, 23.5 pounds (0.165 moles) of technical grade benzoyl chloride and 11.5 pounds (0.165 moles) of technical grade crotonaldehyde. The mixture was then stirred and cooled to 14°F. by circulating cold acetone through the reactor jacket.

A solution of 11.0 pounds of Dupont Cyanegg (equivalent to 0.215 moles of sodium cyanide) in 56.1 pounds of water was then added at such a rate that the temperature could be maintained at about 14°F. This addition required approximately 2 hours during which time the temperature varied from 13°F. to 18°F. Stirring was continued for another 1.5 hours and the mixture allowed to settle. The mixture was then stirred and allowed to settle intermittently until room temperature was reached. The light yellow, clear, aqueous phase was then withdrawn and the product phase was washed twice with 2.8 pound portions of 5 percent sodium carbonate solution. The deep red product layer was then withdrawn, dried over 3 pounds of anhydrous magnesium sulphate for about 16 hours, filtered, and distilled under a vacuum to remove the benzene and toluene. Distillation of the crude product under reduced pressure gave 25.5 pounds (75.5 percent of theoretical) of crotonaldehyde cyanohydrin benzoate, a light yellow liquid boiling at 125-155°C. at 1 to 4 millimeters pressure. The refractive index (n_D^{20}) measured 1.5222 compared to a literature value of 1.5220. The crotonaldehyde cyanohydrin benzoate, to which a small amount of picric acid was added, was pyrolyzed in a one-inch stainless steel tube 4-feet long and packed with 0.25-inch ceramic Berl saddles. After flushing the pyrolysis tube with nitrogen, the ester was charged through a small Milton-Roy pump at the rate of 22 milliliters per minute while the temperature inside of the pyrolysis tube was maintained at 1015-1115°F. The pyrolysate was collected in a 5-liter, round bottom flask equipped with a 5-foot air condenser. The pyrolysis tube tends to clog after the pyrolysis of about 8 to 10 pounds of the ester; however, it was found that the tube may very conveniently and rapidly be burned out with air at any appropriate time.

The crude 1-cyano-1,3-butadiene was then removed from the pyrolysate by vacuum distillation. A temperature of 165°F. and at least 24 hours appeared sufficient to recover most of the desired product from the benzoic acid formed. Picric acid was added both to pyrolysis and distillation receivers to inhibit polymerization. A yield of 1240 grams (68.2 percent of the theoretical) of almost colorless liquid was obtained. The pyrolysate and the recovered cyanobutadiene were stored at dry-ice temperature while waiting further purification.

Separation of the cis and trans-isomers of the 1-cyano-1, 3-butadiene was attempted by fractionation through a 1 inch by 36 inch Podbielniak column at 3.5 millimeters pressure and a reflux ratio of 30 to 1. Relatively pure cis-isomer was obtained, but a purity of only about 75 percent was obtained for the trans-isomer. It is believed that due to the apparently high pressure drop across the column and the long residence time in the pot that most of the trans-isomer had polymerized. The following samples were used for copolymerization:

<u>Sample No.</u>	<u>% Cis-</u>	<u>% Trans-</u>	<u>Total</u>
4842-17-1	98.0	1.0	99.0
4842-17-2	70.6	36.8	107.4
4842-17-3	33.4	76.7	110.1

The concentration of cis and trans-isomers was determined by infrared analysis using samples of the pure isomers obtained from H. R. Snyder at the University of Illinois.

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APPENDIX II

TABLE I

EVALUATION OF VARIOUS POLYBUTADIENES AS PLASTICIZERS IN PARACRIL NS-26

Plasticizer	PHR Plasticizer	% Plasticizer Extracted	% Swell	T-R FP °C	% Cold Relaxed 10 sec	Comp. Set Relaxed 30 min	Remarks
L-1	10	62.4	42.0	-32 ^{a,b}	-	95.9 ^a	
L-1	20	65.0	43.6	-36 ^{a,b}	-	95.3 ^a	
L-1/TP-90B	10/5	69.4	39.3	-39 ^{a,b}	-	87.2 ^a	
4135-92	10	58.8	46.7	-33 ^{a,b}	-	96.4 ^a	
4135-92	20	54.5	48.8	-34 ^{a,b}	-	97.7 ^a	
4135-92/TP-90B	10/5	66.0	42.4	-38 ^{a,b}	-	89.1 ^a	
Serial #5	10	15.7	56.1	-31	-	96.4 ^a	
Serial #5	30	35.3	73.0	-28	-	97.2 ^a	
Serial #5	30 ^c	16.3	57.4	-26	-	97.1 ^a	
TP-90B	10	75.1	33.6	-41 ^{a,b}	-	76.8 ^a	
TP-90B	10	86.0	33.3	-38 ^{a,b}	-	75.0 ^a	
TP-90B	20	76.6	25.9	-47 ^{a,b}	-	46.6 ^a	
TP-90B	30	78.6	18.9	-45	-	31.7 ^a	
4135-92	10	72.6	49.7	-30	96.8	96.5	
4135-92/TP-90B	10/10	76.6	36.8	-39	95.6	71.6	
4135-92/ZL-109	10/10	56.6	39.5	-35	96.8	94.7	
4135-92	20	69.1	49.1	-32	97.0	96.5	
4135-92/TP-90B	20/10	73.8	41.6	-40	94.7	71.1	
4135-92/ZL-109	20/10	63.0	42.8	-35	96.8	93.3	
4135-92	30	77.1	55.2	-32	96.8	96.3	Bled
Ser #5/ZL-109	10/10	37.6	50.2	-33	-	-	
ZL-109	10	32.8	41.6	-33	97.0	95.6	
ZL-109	20	18.4	35.4	-	95.3	92.8	
ZL-109	30	12.9	33.2	-	93.9	88.1	
TP-90B	10	77	38.8	-38	96.6	86.1	
TP-90B	20	88.1	26.3	-45	87.4	45.0	
TP-90B	30	82.5	21.2	-50	75.4	30.9	
---	-	-	48.6	-29	97.1	97.0	
Liq. PBD, 768 Vis.	10	34.0	59.9	-29	97.5	97.2	Slick
Liq. PBD, 768 Vis.	30	58.7	62.4	-29	97.5	97.2	Bled very badly
Liq. PBD, 1037 Vis.	10	29	60.5	-29	98.0	97.5	Slick
Liq. PBD, 1037 Vis.	30	29.3	79.4	-31	97.6	97.1	Bled very badly
TP-90B	10	94	36.4	-36	95.2	78.6	
TP-90B	30	74.2	23.3	-46	74.2	32.8	
---	-	-	43.8	-29	97.3	97.2	

a) 30 minute cure

b) Gehman FPOC

c) 5 phr sulfur

TABLE II
EVALUATION OF POLYBUTADIENE DERIVATIVES AS
PLASTICIZERS IN PARACRIL NS-26

<u>Plasticizer</u>	<u>PHR</u> <u>Plasticizer</u>	<u>%</u> <u>Plasticizer</u> <u>Extracted</u>	<u>%</u> <u>Swell</u>	<u>FP °C</u> <u>(Gehman)</u>	<u>% Cold Comp. Set</u>		<u>Remarks</u>
					<u>Relaxed</u> <u>10 sec</u>	<u>Relaxed</u> <u>30 min</u>	
HB-21	10	23.3*	48.8	-39	-	97.0	10 per cent oxygen
HB-24	10	9.0*	49.2	-40	-	98.8	
HB-34A	10	28.7*	50.2	-41	-	97.0	6.5 per cent oxygen
HB-43	10	18.0*	47.0	-30	-	99.1	20.3 per cent oxygen
HB-44	10	19.7*	47.0	-31	-	99.1	
HB-51	10	0.0*	45.2	-30	-	-	22.0 per cent oxygen
HB-58	10	21.5*	49.3	-30	-	96.2	6.5 per cent oxygen
HB-61	10	5.4*	44.6	-30	-	96.6	
HB-63	10	19.7*	48.8	-29	-	97.0	
HB-67	10	19.7*	45.1	-31	-	94.8	
HB-71H	10	28.7*	52.5	-32	-	98.5	
HB-84	10	21.5*	45.7	-31	-	98.2	
HB-86	10	23.3*	49.3	-31.5	-	-	7.1 per cent oxygen
HB-93	10	1.8*	45.2	-31	-	-	19.5 per cent oxygen
Liq. PBD	10	19.7*	61.9	-42	-	-	
(T-R)							
HB-121	10	42.0	56.3	-30	98.2	97.8	2 per cent oxygen
HB-121	30	38.0	74.9	-30	97.7	97.6	
HF-PBD ₁	10	76.0	42.5	-29	97.7	97.4	
HF-PBD ₁	30	76.0	37.7	-29	98.0	97.7	
HF-PBD ₂	10	64.0	47.5	-29	97.8	97.5	
HF-PBD ₂	30	61.3	48.2	-29	97.8	97.6	
4669-49-B	10	98.0	41.8	-29	97.2	97.0	
4669-49-B	30	100.0	19.5	-29	97.4	97.2	Bled slightly
4669-49-C	10	123	38.6	-28	97.7	97.3	
4669-49-C	30	98.0	22.8	-27	97.6	97.6	Bled slightly
TP-90B	10	76.0	39.8	-37	97.2	86.7	
TP-90B	30	80.7	22.3	-48	72.8	30.4	
---	-	-	48.4	-29	97.1	96.8	
4618-58	10	47.5	51.8	-32	97.1	96.8	9.2 per cent oxygen
4618-58	30	36.6	64.5	-32	97.2	96.8	
TP-90B	10	92.5	38.8	-42	93.5	75.7	
TP-90B	30	82.5	22.5	-46	71.9	29.0	

*Aliquot Method

TABLE III
DESCRIPTION OF POLYBUTADIENE AND
POLYBUTADIENE DERIVATIVES

<u>Code No.</u>	<u>Description</u>
L-1	Sodium-polymerized liquid polybutadiene precipitated to give a low viscosity fraction (30 Saybolt Furol seconds viscosity).
4135-92	Hydrogenated low viscosity liquid polybutadiene corresponding to L-1 (15.9 per cent unsaturation).
Serial #5	Sodium-polymerized liquid polybutadiene (460 Saybolt Furol seconds viscosity).
Liq. PBD, 768 Vis.	Sodium-polymerized liquid polybutadiene (768 Saybolt Furol seconds viscosity).
Liq. PBD, 1037 Vis.	Sodium-polymerized liquid polybutadiene (1037 Saybolt Furol seconds viscosity).
HB-21	Hydroxypolybutadiene (10 per cent oxygen).
HB-24	Hydroxypolybutadiene.
HB-34A	Hydroxypolybutadiene (6.5 per cent oxygen).
HB-43	Hydroxypolybutadiene (20.3 per cent oxygen).
HB-44	Acetylated hydroxypolybutadiene.
HB-51	Hydroxypolybutadiene (22.0 per cent oxygen).
HB-58	Oxidized polybutadiene (6.5 per cent oxygen).
HB-61	Phosphate ester of hydroxypolybutadiene and butanol.
HB-63	Oleate of hydroxypolybutadiene.
HB-67	Hydroxypolybutadiene condensed with ethylene oxide.
HB-71H	Hydrogenated, air-oxidized polybutadiene.
HB-84	Formate of hydroxypolybutadiene.
HB-86	Hydroxypolybutadiene (7.1 per cent oxygen).
HB-93	Hydroxypolybutadiene (19.5 per cent oxygen).
HB-121	Hydroxypolybutadiene (2 per cent oxygen).
HF-PBD ₁	Hydrogen fluoride-polymerized liquid polybutadiene.
HF-PBD ₂	Same as HF-PBD ₁ except different purification procedure.
4669-49-B	Vinylcyclohexene (butadiene dimer) polymer-overhead product.
4669-49-C	Vinylcyclohexene polymer - pot residue.
4618-58	Oxidized Serial #8 liquid polybutadiene (9.2 per cent oxygen).
ZL-109	A Thiokol liquid polysulfide.
TP-90B	Di-(butyl Carbitol) formal.

TABLE IV
EVALUATION OF BUTADIENE-PURFURAL COPOLYMERS
AS PLASTICIZERS IN PARACRIL NS-26

<u>Plasticizer</u>	<u>PHR</u> <u>Plasticizer</u>	<u>%</u> <u>Plasticizer</u> <u>Extracted</u>	<u>%</u> <u>Swell</u>	<u>T-R</u> <u>FP °C</u>	<u>% Cold</u> <u>Comp. Set</u> <u>Relaxed</u> <u>30 min</u>
BF-1	10	55.2	37.8	-40	94.8
BF-1	30	75.1	21.8	-43	82.7
BF-2	10	37.7	41.6	-26.7 ^a	-
BF-1	10	102.5	34.7	-34	94.7
BF-1	30 ^b	87.2	19.8	-37	80.1
BF-3	10	91.6	34.5	-32	94.9
BF-3	30 ^b	81.3	20.4	-35	81.4
BF-4	10	88.1	35.1	-33	95.4
BF-4	30 ^b	83.8	20.1	-36	79.7
BF-5	10	89.6	34.9	-32	95.9
BF-5	30 ^b	79.0	21.2	-34	89.6
BF-1/TP-90B	10/5	74.0	32.7	-39	85.1
BF-1/TP-90B	10/10	85.5	26.4	-41	69.7
BF-1/TP-90B	10/15	82.1	21.8	-41	60.8
BF-1	10	81.0	26.8	-37	95.3 ^c
BF-1	20	81.6	26.9	-38 ^{a, c}	87.6 ^c
BF-1	30	81.2	20.9	-38	81.9 ^c
BF-1	30 ^d	73.9	17.5	-34	81.8 ^c
BF-7	10	81.0	34.6	-33 ^{a, c}	95.2 ^c
BF-7	20	76.6	26.9	-34 ^{a, c}	94.2 ^c
BF-8	10	60.6	35.8	-34 ^{a, c}	95.9 ^c
BF-8	20	70.0	27.6	-34 ^{a, c}	92.4 ^c
HBF-1	10	0.0	40.2	-28 ^{a, c}	95.1 ^c
HBF-1	20	5.0	36.7	-27 ^{a, c}	95.9 ^c
HBF-2	20	2.5	37.8	-27 ^{a, c}	95.7 ^c
TP-90B	10	75.1	33.6	-41 ^{a, c}	76.8 ^c
TP-90B	10	86.0	33.3	-38	75.0 ^c
TP-90B	20	76.6	25.9	-47 ^{a, c}	46.6 ^c
TP-90B	30	78.6	18.9	-45	31.7 ^c

- a) Gehman FP °C
b) 2.0 phr Altax
c) 30 minute cure
d) 5.0 phr sulfur

TABLE V
DESCRIPTION OF BUTADIENE-FURFURAL COPOLYMERS

<u>Code No.</u>	<u>Description</u>
BF-1	Purified 2,3,4,5-bis-(Δ^2 -butenylene) tetrahydrofurfural.
BF-2	Crude tar from butadiene plant containing approximately 15 per cent BF-1 and other condensation products.
BF-3	Overhead from partial stripping of crude tar with 400 F steam.
BF-4	Overhead from stripping BF-5 again with 400 F steam.
BF-5	Overhead from complete stripping of crude tar with 400 F steam using vacuum during the final stages.
BF-7	2,3,4,5-bis (Δ^2 -butenylene) tetrahydrofurfuryl alcohol.
BF-8	Product from the condensation of ethylene oxide with BF-7 in a mol ratio of 4 to 1.
HBf-1	Hydroxylated and polymerized BF-1.
HBf-2	Hydroxylated BF-7.

TABLE VI
EVALUATION OF HYDROXYLATED BUTADIENE
DERIVATIVES AS PLASTICIZERS IN PARACRIL NS-26

<u>Plasticizer</u>	<u>PHR</u> <u>Plasticizer</u>	<u>%*</u> <u>Plasticizer</u> <u>Extracted</u>	<u>%</u> <u>Swell</u>	<u>Gehman</u> <u>FP °C</u>	<u>% Cold</u> <u>Comp. Set</u> <u>Relaxed</u> <u>30 min</u>
HB-53E	10	0.0	44.2	-30.5	98.8
HB-54E	10	71.8	23.2	-34	96.2
ED-1	10	10.8	46.2	-30	99.1
ED-2	10	91.5	38.5	-32	99.1
ESD-1	10	97.0	38.6	-32	100.0
ESD-2	10	84.3	39.5	-32	99.4
ED-3	10	53.2	40.9	-32	98.5
ED-4	10	0.0	45.9	-31	98.5
ED-5	10	9.0	45.9	-32	98.5

*Aliquot method

HB-53E: Residues from erythritol preparation
 HB-54E: Erythritol tetrabutyrates
 ED-1: Polyester of erythran and sebacic acid
 ED-2: Erythritol laurate
 ESD-1: Pentaerythritol laurate
 ESD-2: Glycerol laurate
 ED-3: Erythritol tartrate (+ cyclohexanone)
 ED-4: Polyester of 3-butene-1,2-diol and succinic acid
 ED-5: Polyester of 3-butene-1,2-diol and adipic acid

TABLE VII
EVALUATION OF POLYETHYLENE GLYCOL DERIVATIVES
AS PLASTICIZERS IN PARACIL NS-26

<u>Plasticizer</u>	<u>PHR</u> <u>Plasticizer</u>	<u>%</u> <u>Plasticizer</u> <u>Extracted</u>	<u>%</u> <u>Swell</u>	<u>T-R</u> <u>FP °C</u>	<u>% Cold Comp. Set</u>		<u>Remarks</u>
					<u>Relaxed</u> <u>10 sec</u>	<u>Relaxed</u> <u>30 min</u>	
4419-77	10	75.0	34.4	-35	-	92.4 ^a	
4419-77	30	76.6	20.2	-40	-	38.2 ^a	Bled
4618-19	10	64.3	35.3	-37	-	95.5 ^a	
4618-19	30	68.6	22.6	-38	-	94.5 ^a	Bled
4618-26	10	71.4	34.9	-35	-	95.4 ^a	Bled
4618-26	30	67.0	24.4	-35	-	81.7 ^a	Bled
4618-25	10	30.0	40.0	-30	-	97.4	Bled
4618-25	30	34.0	33.2	-28	-	96.8	Bled
TP-90B	10	86.0	33.3	-38	-	75.0 ^a	
TP-90B	30	78.6	18.9	-45	-	31.7 ^a	
4618-28	10	90.5	36.2	-38	96.8	90.9	
4618-28	30	80.7	23.1	-39	92.9	48.0	Bled
4618-49	10	90.5	35.8	-38	96.7	89.2	
4618-49	30	66.7	26.6	-40	95.1	65.2	Bled
4618-70	10	74.5	38.5	-34	96.3	95.0	
4618-70	30	68.7	24.3	-38	96.1	85.5	
TP-90B	10	92.5	38.8	-42	93.5	75.7	
TP-90B	30	82.5	22.5	-46	71.9	29.0	
4618-71-2	10	68	39.5 ^b	-31	97.1 ^c	96.7 ^c	
4618-71-2	30	84.5	26.3 ^b	-31	96.5 ^c	96.2 ^c	Bled
TP-90B	10	77	38.8 ^b	-38	96.6 ^c	86.1 ^c	
TP-90B	30	82.5	21.2 ^b	-50	75.4 ^c	30.9 ^c	
---	-	-	48.6 ^b	-29	97.1 ^c	97.0 ^c	

a) 30 minute cure.

b) Two days in 70/30 isooctane-toluene at 158 F then dried 3 days at 150 F.

c) In carbon dioxide atmosphere.

TABLE VIII

DESCRIPTION OF POLYETHYLENE GLYCOL DERIVATIVES

<u>Code No.</u>	<u>Description</u>
4419-77	Product from the reaction of equimolar quantities of Polyethylene Glycol 200 and caprylic acid.
4618-19	Product from the reaction of equimolar quantities of Polyethylene Glycol 400 and caprylic acid.
4618-26	Blend containing 42 per cent Polyethylene Glycol 200, 24 per cent 4419-77 and 29 per cent 4618-19.
4618-25	Product from the reaction of Polyethylene Glycol 200 with sebacic acid in a mol ratio of 2 to 1.
4618-28	Polyethylene Glycol 200 monobutyrate.
4618-49	The β -cyanoethyl ether of Polyethylene Glycol 200 monobutyrate.
4618-70	Mixed adipate of butyl Carbitol and Polyethylene Glycol 200.
4618-71-2	The di(β -cyanoethyl) ether of Polyethylene Glycol 200.

TABLE IX

EVALUATION OF BLENDS OF ZL-109 AND TP-90B AS PLASTICIZERS IN PARACRIL NS-26

ZL-109 TP-90B (phr)	Compounded MS-14 at 212 F	Tensile (psi)	% Elongation	Shore Hardness	% Swell	% Plasticizer Extracted	212 F Comp, Set	T-R FP (C)	% Cold Comp. Relaxed 10 sec	Set** Relaxed 30 min
0/10	33.5	3260	280	64	35E	38	9.2	-37	95.8	76.9
0/15	26.5	2690	265	61.5	29.7	98.0	9.3	-44	93.4	56.2
0/20	23.5	2760	285	58.5	26.3	92.0	10.5	-46	84.1	44.1
0/30	16	2380	295	57.5	19.4	89.8	11.8	-51	71.0	30.7
10/0	53.5	2820	240	69	41.6	32.8	13.9	-33	97.0	95.6
20/0	35.5	2380	150	76	35.6	23.5	15.0	a	94.9	92.6
30/0	32	1610	085	79	33.1	14.3	13.8	a	93.4	88.2
40/0	25.5	1470	075	78.5	31.3	11.0	13.2	a	93.2	83.4
10/10	47.5	2880	335	60	33.6	56.6	29.3	-40	95.1	71.1
20/10	28.5	2535	220	66	30.8	45.0	21.2	-43	89.3	37.5 e
20/15	25.5	2510	260	62	26.3	53.2	24.4	-47	79.2	29.1 b
20/0 f	38.5	2960	160	75	34.6	24.0	15.0	a	95.3	93.2
20/10 f	27.5	2950	280	65.5	30.6	47.0	22.4	-42	90.0	40.6
20/15 f	23.5	2460	260	60.5	26.6	53.7	25.1	-45	86.6	31.4 c
30/10 f	20	1850	135	71	26.4	32.2	21.3	a	87.6	22.0
40/10 f	18	1420	095	73	23.7	28.8	23.3	a	87.4 d	16.6
---	63	2875	220	71	46.2	---	7.0	-26	96.6	96.6
----f	61.5	3710	245	72	44.3	---	7.1	-25	96.5	96.5

* Two days in 70/30 isooctane-toluene at 158 F and oven dried 3 days at 158 F.

** In CO₂ atmosphere.

c) Samples broke either when elongated or when placed in liquid.

b) 23.5 per cent at 75 minutes cure.

c) 24.6 per cent at 75 minutes cure.

d) 54.8 per cent at approximately one minute relaxation.

e) 32.5 per cent at 75 minutes cure.

f) 2.5 phr sulfur and 2.0 phr Altax.

TABLE X

EVALUATION OF AMIDE-TYPE PLASTICIZERS IN PARACRIL NS-26

Plasticizer	PHR Plasticizer	% Plasticizer Extracted	% Swell	T-R FP °C	% Cold Comp. Set	
					Relaxed 10 sec	Relaxed 30 min
N-8U/TP-90B	5/5	63	37.1	-38	96.6	95.1
N-8U/TP-90B	5/10	71.5	32.0	-42	95.8	80.6
N-8U/TP-90B	10/10	72.6	27.7	-37	95.4	87.4
N-8U	10	58.3	39.9	-34	95.9	95.4
N-8U	20	67.2	31.8	-27	95.8	95.1
N-8U/TP-90B	20/10	73.8	24.0	-37	95.7	90.2
N-8U	30	72.5	28.7	-29	96.4	96.2
TP-90B	10	98	36.2	-38	96.5	79.7
TP-90B	30	81.1	22.1	-50	72.8	29.9
----	--	-	47.2	-30	96.9	96.7
4843-17	10	18	73.9 ^a	-29	97.1 ^b	96.9 ^b
4843-17	30	15.3	41.3 ^a	-28	97.2 ^b	97.1 ^b
TP-90B	10	94	36.4 ^a	-36	95.2 ^b	78.6 ^b
TP-90B	30	74.7	23.3 ^a	-46	74.2 ^b	37.8 ^b
----	-	-	43.8 ^a	-29	97.3 ^b	97.2 ^b
4843-25	10	55 ^a	40.7 ^a	-38	96.7 ^b	88.6 ^b
4843-25	30	54.3 ^a	31.7 ^a	-45	89.8 ^b	38.6 ^b
4843-23	10	62 ^a	41.1 ^a	-33	96.8 ^b	95.4 ^b
4843-23	30	83.7 ^a	26.1 ^a	-34	97.8 ^b	97.2 ^b
TP-90B	10	88 ^a	36.0 ^a	-40	95.8 ^b	78.7 ^b
TP-90B	30	79.0 ^a	20.5 ^a	-51	78.0 ^b	31.4 ^b
----	-	-	46.3 ^a	-29	97.1 ^b	97.1 ^b
4843-21	10	81 ^a	40.5 ^a	-c	97.7 ^b	97.4 ^b
4843-21	30	86.0 ^a	27.6 ^a	-c	97.4 ^b	97.2 ^b
TP-90B	10	96 ^a	37.4 ^a	-c	95.6 ^b	75.5 ^b
TP-90B	30	84.0 ^a	19.8 ^a	-c	70.1 ^b	29.5 ^b
----	-	-	47.3 ^a	-c	96.9 ^b	96.8 ^b

Bled
Bled badly

Bled

- a) Two days in 70/30 isooctane-toluene at 158 F then dried 3 days at 150 F.
 b) In carbon dioxide atmosphere.
 c) Freeze points are not yet available.

TABLE XI
DESCRIPTION OF AMIDE-TYPE PLASTICIZERS

<u>Code No.</u>	<u>Description</u>
N-8U	n-Octyl urea
4843-17	Diethanolformamide
4843-25	N-formyl morpholine
4843-23	Sym-N,N'-diethanolurea
4843-21	β -hydroxyethylurethan

TABLE XII
EVALUATION OF TP-90B DERIVATIVES AS PLASTICIZERS
IN PARACRIL NS-26

<u>Plasticizer</u>	<u>PHR Plasticizer</u>	<u>% Plasticizer Extracted</u>	<u>% Swell</u>	<u>FP °C</u>		<u>% Cold Comp. Set Relaxed 30 min</u>
				<u>T-R</u>	<u>Gehman</u>	
NES-1	10	40.8	37.3	-	-37 ^a	93.3
NES-1	20	41.0	30.6	-	-40 ^a	78.4
4618-9	10	95.0	32.4	-41	-39	79.4
4618-9	30	83.3	17.3	-45	-51	31.9
TP-90B	10	75.1	33.6	-	-41 ^a	76.8
TP-90B	10	86.0	33.3	-38	-42	75.0
TP-90B	20	76.6	25.9	-	-47 ^a	46.6
TP-90B	30	78.6	18.9	-45	-55	31.7

a) 30 minute cure

NES-1: Product from the reaction of TP-90B with m-tolylene diisocyanate.
4618-9: Product from the reaction of TP-90B with succinic anhydride.

TABLE XIII
EVALUATION OF HYDROXYNITRILES AS PLASTICIZERS
IN PARACRIL NS-26

<u>Plasticizer</u>	<u>PHR Plasticizer</u>	<u>% Plasticizer Extracted</u>	<u>% Swell</u>	<u>T-R FP °C</u>	<u>% Cold^a Comp. Set Relaxed 30 min</u>
4419-81	10	79.0	34.6	-34	95.4
4419-81	30	74.6	20.7	-35	91.2
4618-10	10	79.0	34.6	-36	96.6
4618-10	30	76.0	20.8	-41	92.7
TP-90B	10	86.0	33.3	-38	75.0
TP-90B	30	78.6	18.9	-45	31.7

a) 30 minute cure

4419-81: Hydroxylated Arneel TOD
4618-10: Hydroxylated Arneel SD

TABLE XIV
EVALUATION OF VULCANIZABLE PLASTICIZERS IN PARACRIL NS-26

<u>Plasticizer</u>	<u>PHR Plasticizer</u>	<u>% Plasticizer Extracted</u>	<u>% Swell</u>	<u>T-R FP °C</u>	<u>% Cold Comp. Set Relaxed 10 sec</u>	<u>Relaxed 30 min</u>
DAS	10	73.2	35.8	-40	-	80.9
DAS	30	83.3	18.9	-49	-	96.2
DAS	30 ^a	83.3	18.1	-51	-	96.7
DAS	30 ^b	81.7	19.8	-47	-	96.6
DAS ^c	10	66.5	40.6	-32	-	88.3
DAS ^c	30	21.3	42.3	-31	-	82.4
DAS ^c	30 ^a	22.1	41.1	-30	-	83.0
DAS ^c	30 ^b	-	45.8	-28	-	-
DVB	5	23.4	46.5	-30	97.4	96.9
DVB/TP-90B	5/5	56.5	42.1	-35	96.9	91.3
DVB	10	34.8	44.8	-36	97.4	96.1
DVB/TP-90B	10/10	59.6	32.1	-40	94.8	71.5
DVB	30	22	41.3	-36	96.4	92.8
TP-90B	10	98	36.2	-38	96.4	79.7
TP-90B	30	81.1	22.1	-50	72.8	29.9
---	-	-	47.2	-30	96.9	96.7

a) One part benzoyl peroxide added.

b) One part benzoyl peroxide added, then treated 8 hrs. at 120 F and 2 hrs. at 212 F.

c) Extracted stock.

DAS: Diallyl sebacate

DVB: Divinyl benzene

TABLE XV

EVALUATION OF SILICONES AS PLASTICIZERS IN PARACRIL NS-26

<u>Plasticizer</u>	<u>PHR Plasticizer</u>	<u>% Plasticizer Extracted</u>	<u>%^a Swell</u>	<u>T-R FP °C</u>	<u>% Cold Comp. Set^b</u>		<u>Remarks</u>
					<u>Relaxed 10 sec</u>	<u>Relaxed 30 min</u>	
4209-34-1	10	0.0	66.9	-28	97.8	97.5	Bled
4209-34-1	30	6.7	85.4	-25	97.7	97.5	Bled badly
4209-34-2	10	6.0	63.4	-27	97.8	97.6	Slick
4209-34-2	30	22.7	70.3	-26	97.3	97.2	Bled
TP-90B	10	94	36.4	-36	95.2	78.6	
TP-90B	30	74.7	23.3	-46	74.2	37.8	
----	-	-	43.8	-29	97.3	97.2	

a) Two days in 70/30 isooctane-toluene at 158 F then dried 3 days at 158 F.

b) In carbon dioxide atmosphere.

4209-34-1: Experimental silicone plasticizer (Dow-Corning stopcock grease).

4209-34-2: Experimental silicone plasticizer (Dow-Corning anti-foam A).

TABLE XVI

EVALUATION OF PHOSPHONATES AS PLASTICIZERS IN PARACRIL NS-26

<u>Plasticizer</u>	<u>PHR Plasticizer</u>	<u>%^a Plasticizer Extracted</u>	<u>%^a Swell</u>	<u>% Cold Comp. Set^b</u>	
				<u>Relaxed 10 sec</u>	<u>Relaxed 30 min</u>
4209-35-1	10	94	37.6	96.8	95.9
4209-35-1	30	96.0	18.9	95.4	67.2
4209-35-2	10	92	38.0	97.1	96.4
4209-35-2	30	93.4	19.0	96.8	85.1
TP-90B	10	96	37.4	95.6	75.5
TP-90B	30	84.0	19.8	70.4	29.5
----	-	-	47.3	96.9	96.8

Note: Freeze points not yet available.

a) Two days in 70/30 isooctane-toluene at 158 F then dried 3 days at 158 F.

b) In carbon dioxide atmosphere.

4209-35-1: Diisooctyl phenylphosphonate.

4209-35-2: Diisooctyl styrylphosphonate.

TABLE XVII

EVALUATION OF MISCELLANEOUS PLASTICIZERS IN PARACRIL NS-26

Plasticizer	PHR Plasticizer	% Plasticizer Extracted	% Swell	T-R FP °C	% Cold Comp. Set	
					Relaxed 10 sec	Relaxed 30 min
AP-65	10	52.1 ^a	39.0	-32 ^b	-	97.7
AP-M	10	-	38.6	-33 ^b	-	94.2
Sorbitol	5	16.4	44.8	-27	95.9	95.3
Sorbitol	10	14.9	46.2	-28	96.6	96.5
Sorbitol/TP-90B	10/10	47	36.9	-35	96.3	87.0
Sorbitol/TP-90B	30/10	30.3	31.5	-35	96.6	91.8
Sorbitol	30	12.4	38.7	-27	97.1	96.9
TP-90B	10	98	36.2	-38	96.5	79.7
TP-90B	30	81.1	22.1	-50	72.8	29.9
-----	-	-	47.2	-30	96.9	96.7

a) Aliquot method

b) Gehman FPOC

AP-65: Mercaptan-ethylene oxide (9 moles)

AP-M: Mercaptan-ethylene oxide (1 mol)

TABLE XVIII

POLYMERIZATION DETAILS OF 90/10 BUTADIENE/CIS-1-CYANOBUTADIENE COPOLYMERS

Sample	1-Cyanobutadiene Composition			Parts DDM	Polym. Time Hrs.	% Conv.	Wt. Polymer (gms)	Mooney ML-4
	% Cis	% Trans	Total %					
4936-2-1	98.0	1.0	99.0	0.355	11	60.1	130	125
4936-6-1	98.0	1.0	99.0	0.45	10.5	63.9	150	108
4936-6-2	70.6	36.8	107.4	0.40	11.75	56.2	30	95
4936-6-3	33.4	76.7	110.1	0.40	22.5	62.0	30	101
4936-8-1	70.6	36.8	107.4	0.75	11.5	64.3	165	75
4936-10-1	33.4	76.7	110.1	0.70	16	62.6	130	59
4936-10-2	33.4	76.7	110.1	0.70	16	68.5	67	58
4936-11-1	98.0	1.0	99.0	0.70	10	68.4	116	81
4936-11-2	98.0	1.0	99.0	0.70	11	62.3	46	70
4936-11-3	70.6	36.8	107.4	0.70	11	63.4	81	
4936-11-4	70.6	36.8	107.4	0.70	11	62.4	20	55

TABLE XIX

EVALUATION OF 90/10 BUTADIENE/1-CYANOBUTADIENE COPOLYMERS AS OIL RESISTANT RUBBERS
(30 Minutes Cure at 307°F)

Elastomer	Plasticizer (20 PHR)	80°F		200°F		80°F		200°F		80°F		Shore Hardness	212°F Compression Set, (%)	T-T FP, (C)	% Cold Comp. Set ^a Relaxed		Compounded MS-14 at 212°F
		303, Modulus (psi)	Tensile (psi)	Elongation (%)	Maximum Tensile (psi)	Tensile (psi)	Elongation (%)	Tensile (psi)	Elongation (%)	10 sec.	30 min.						
															(Oven Aged 24 hours at 212 F)		
CNBD-1	TP-90B	—	1810	160	1040	1600	130	1600	1600	130	70	9.8	-65	60.9	31.8	52	
CNBD-1	Liq. PBD	—	1860	210	840	1520	120	1520	1520	120	70	13.1	-45	93.8	87.0	43.5	
Paracrill 18	TP-90B	—	2580	285	1240	2860	230	2860	2860	230	61	10.0	-54	75.3	37.0	17	
Paracrill 18	Liq. PBD	2060	2320	335	940	2300	265	2300	2300	265	62.5	10.0	-40	95.9	81.7	20	
Paracrill B	TP-90B	2700	3020	335	1600	3150	265	1600	3150	265	63	14.1	-46	89.3	47.9	16	
Paracrill B	Liq. PBD	1980	2320	345	1060	2310	270	1060	2310	270	64	13.1	-30	97.4	97.1	12.5	
CNBD-2	TP-90B	—	1340	190	900	1840	140	900	1840	140	61.5	13	<-55	69.2	38.7	34	
CNBD-2	Liq. PBD	—	750	190	600	1500	210	600	1500	210	57	13.3	<-60	95.9	94.8	34	
CNBD-3	TP-90B	—	1500	190	880	1950	160	880	1950	160	63	13.7	<-40	68.6	36.8	44.5	
CNBD-3	Liq. PBD	—	690	170	340	1480	215	340	1480	215	58	13.6	<-45	96.0	93.8	35.5	
CNBD-4	TP-90B	—	1570	190	860	1900	170	860	1900	170	64.5	11.3	<-65	60.8	31.1	44.5	
Paracrill 18	TP-90B	—	2520	295	1660	2610	195	1660	2610	195	63	10.5	-54	71.5	38.7	26	
Paracrill 18	Liq. PBD	—	1680	290	860	2410	280	860	2410	280	61.5	10.9	-40	95.3	85.0	19	
Paracrill B	TP-90B	2770	3160	340	1535	3230	220	1535	3230	220	64	7.4	-46	82.6	45.0	28	
Paracrill B	Liq. PBD	1500	1830	350	760	1910	260	760	1910	260	62	12.5	-32	96.5	96.1	28	

a) In carbon dioxide atmosphere.

CNBD-1 Blend of 1 part of 4936-2-1 and 2 parts of 4936-6-1 (90/10 butadiene/cis-1-cyanobutadiene - see Table XVIII).
 CNBD-2 Blend of 124 g of 4936-10-1 and 60 g of 4936-10-2 (90/10 butadiene/trans-1-cyanobutadiene - see Table XVIII).
 CNBD-3 Blend of 165 g of 4936-8-1 and 96 g of 4936-11-3⁴ (90/10 butadiene/cis-2, trans-1-cyanobutadiene - see Table XVIII).
 CNBD-4 Blend of 108 g of 4936-11-1 and 36 g of 4936-11-2 (90/10 butadiene/cis-1-cyanobutadiene - see Table XVIII).

TABLE XX

EVALUATION OF 90/10 BUTADIENE/1-CYANOBTADIENE COPOLYMERS AS OIL RESISTANT RUBBERS

SUMMARY OF SWELL AND EXTRACTION PROPERTIES^a

Elastomer	Plast. cizer	Minutes	Specific Gravity	70/30 Isooctane/Toluene		Isopentane		ASTM Oil #3
				% Swell	% Extracted	% Swell	% Extracted	% Swell
CNBD-1	TP-90B	30	1.144	80.8	14.3	27.2	22.8	26.0
CNBD-1	TP-90B	75	1.182	28.0	10.5	19.9	-	64.5
CNBD-1	Liq. PBD	30	1.137	110.1	11.5	21.8	37.2	-
Paracrill 18	TP-90B	30	1.165	43.7	13.4	25.4	0.1	92.6
Paracrill 18	Liq. PBD	30	1.159	75.1	7.8	14.8	20.4	17.9
Paracrill B	TP-90B	30	1.180	27.2	11.2	21.2	-5.1	38.5
Paracrill B	Liq. PBD	30	1.173	66.5	4.8	9.11	18.0	3.5
								21.7
CNBD-2	TP-90B	30	-	114.9	12.8	24.3	42.8	22.0
CNBD-2	TP-90B	75	-	110.8	12.7	24.1	42.5	86.3
CNBD-2	Liq. PBD	30	-	145.0	12.8	24.3	61.1	22.0
CNBD-2	Liq. PBD	75	-	147.8	12.5	23.8	61.1	20.3
CNBD-3	TP-90B	30	-	110.5	12.9	24.5	38.6	19.9
CNBD-3	TP-90B	75	-	110.3	12.8	24.3	41.6	22.6
CNBD-3	Liq. PBD	30	-	146.8	13.0	24.7	59.6	21.8
CNBD-3	Liq. PBD	75	-	149.8	12.3	23.4	62.1	20.1
CNBD-4	TP-90B	30	-	107.2	12.4	23.6	40.1	19.9
CNBD-4	TP-90B	75	-	106.8	12.3	23.4	40.0	22.2
Paracrill 18	TP-90B	30	-	43.0	13.1	24.9	0.4	22.4
Paracrill 18	TP-90B	75	-	43.7	13.0	24.7	0.1	21.3
Paracrill 18	Liq. PBD	30	-	75.8	8.5	16.2	27.0	21.8
Paracrill 18	Liq. PBD	75	-	72.3	8.5	16.2	26.0	11.0
Paracrill B	TP-90B	30	-	30.5	11.1	21.1	-6.1	11.4
Paracrill B	TP-90B	75	-	26.9	10.7	20.3	-5.7	19.8
Paracrill B	Liq. PBD	30	-	66.4	5.5	10.5	24.3	3.5
Paracrill B	Liq. PBD	75	-	62.7	5.4	10.3	23.2	20.1
								6.6

a) Immersed in fluid 2 days at 158 F and oven dried 3 days at 158 F.
 CNBD-1: Blend of 1 part of 4936-2-1 and 2 parts of 4936-6-1 (cis).
 CNBD-2: Blend of 124 g of 4936-10-1 and 60 g of 4936-10-2 (trans).
 CNBD-3: Blend of 105 g of 4936-8-1 and 96 g of 4936-11-3,4 (cis-trans).
 CNBD-4: Blend of 108 g of 4936-11-1 and 36 g of 4936-11-2 (cis).

TABLE XII

TEMPERATURE RETRACTION DATA FOR 90/10 BUTADIENE/1-CYANO BUTADIENE COPOLYMERS
(30 Minutes Cure at 307 F - Temperature in negative degrees centigrade)

<u>Elastomer</u>	<u>Plasticizer</u> (20 PHR)	<u>T-1</u>	<u>T-3</u>	<u>T-5</u>	<u>T-10</u>	<u>T-20</u>	<u>T-30</u>	<u>T-40</u>	<u>T-50</u>	<u>T-60</u>	<u>T-70</u>	<u>T-80</u>	<u>T-90</u>
CNBD-2	TP-90B	-	65	58	54	49	46	43	39	35	30.5	24	-
CNBD-3	TP-90B	-	69.5	65	57	52.5	48	46	43	39.5	35.5	31	20.5
CNBD-4	TP-90B	-	-	72	61	55	50.5	47.5	44.5	41	37	32	20
Paracrill 18	TP-90B	72	54.5	53	51	48.5	46.5	44	41	37	31.5	-	-
Paracrill B	TP-90B	72	46	44	42	39.5	37.5	36	34.5	31.5	26	-	-
CNBD-2	Liq. PBD	-	48	40	33	27	23	21	18	15	11.5	7	6
CNBD-3	Liq. PBD	-	60	49	40	33	29	25	23	19	15	9	-
Paracrill 18	Liq. PBD	72	41	39	36.5	34	31.5	28.5	26	21	11	-	-
Paracrill B	Liq. PBD	72	31.5	30	28.5	26	24	22.5	19.5	10	-	-	-

CNBD-2: Blend of 124 g of 4936-10-1 and 60 g of 4936-10-2 (trans).

CNBD-3: Blend of 165 g of 4936-8-1 and 96 g of 4936-11-3,4 (cis-trans).

CNBD-4: Blend of 108 g of 4936-11-1 and 36 g of 4936-11-2 (cis).

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